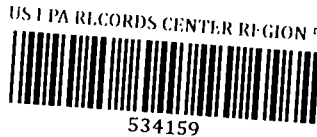


9/12/85
A. 2



Diamond Shamrock
Chemicals Company



RECEIVED
SEP 18 1985

September 12, 1985

U.S. EPA, REGION V
WASTE MANAGEMENT DIVISION
OFFICE OF THE DIRECTOR

Director
Waste Management Division
U. S. Environmental Protection Agency
Region V (5HE-12)
230 S. Dearborn Street
Chicago, Illinois 60605

RE: Consent Order C80-1857
Painesville Site
Action Level Calculation

Dear Sir:

As required by Section III.6 of the above-referenced Consent Order, Diamond Shamrock has calculated the Action Level for hexavalent chromium in the Grand River. As supported by the method of calculation and computations contained in the attached statistical summary, the Action Level has been determined to be 0.06 ppm.

As discussed, the Consent Order does not specify how detectable levels of hexavalent chromium, upstream of the site, will be handled with regard to comparing the downstream average concentration to the Action Level. It is possible, therefore, to be forced into contingency action, solely based upon upstream conditions. In the event that upstream samples indicate greater than detection levels of hexavalent chromium, we propose that the Action Level comparison be based upon a net value of the upstream and downstream analytical results.

If you have any questions regarding the calculation of the action level or proposal for handling upstream data indicating greater than detection level hexavalent chromium, please call me at (713) 476-1405.

Very truly yours,

Thomas J. Stang
Senior Environmental Engineer
Environmental and Safety Services

TJS/sdl
Attachment

Copy To:

Mr. Steve Tuckerman
Ohio Environmental Protection Agency
NEDO
2110 East Aurora Road
Twinsburg, Ohio 44087

Chief, Division of Solid and Hazardous
Waste Management
Ohio Environmental Protection Agency
361 East Broad Street
Columbus, Ohio 43215

Mr. Dan Hopkins
CERCLA Enforcement Section (5HE-12)
U.S. Environmental Protection Agency
Region V
230 S. Dearborn Street
Chicago, Illinois 60604

Diamond Shamrock is tasked by the EPA with monitoring the Grand River adjacent to the old Painesville Chromium Plant site. Enclosure 1 is a copy of the part of the Administrative Consent Order pertaining to the calculation of the "Action Level". This report discusses the statistical interpretation of the rules regarding the analysis of the observations generated from the sampling plan and gives the results of the analysis on the currently available data.

Using the first two years data, from 11 August 1983 to 9 July 1985, the calculated Action Level is .0575 ppm of hexavalent chromium.

INTERPRETATION OF THE REGULATION AND CALCULATION OF THE ACTION LEVEL

Paragraph 5 of Enclosure 1 says in part

"An average hexavalent chromium value will be calculated for the three (3) grab samples at the downstream location for each day of sampling... A one-tailed Students 't' test shall be applied to the logarithms of these values...in order to determine the upper 95 percent confidence limit value (t95). This value shall represent an "Action Level" for hexavalent chromium."

Table 1 lists the data used in the calculation of the Action Level. For the statistical calculations, values less than the detection limit of .01 ppm were replaced by one-half the detection limit (.005). Then, following the regulation, the three samples for each day were averaged and the (natural) logarithm for each daily mean was obtained. Thus, we obtained 23 observations.

Relating the wording concerning the t-test to the calculation of the Action Level yields the following formula for the Action Level. The Action Level equals

$$\exp[\bar{x} + t * s \sqrt{1 + 1/n}] \quad (1)$$

where \bar{x} and s are the mean and standard deviation, respectively, of the logarithms of the n daily means, and t is the upper 95th percentile of the t distribution with $n-1$ degrees of freedom.

From the data in Table 1, the following sample statistics were calculated:

$$\bar{x} = -4.22669 \quad \text{and} \quad s = .781330$$

Further, with $n = 23$, we obtain $t = 1.717$. Thus, for hexavalent chromium, the Action Level is

$$\begin{aligned} & \exp[-4.22669 + 1.717 \times .78133 \sqrt{1 + 1/23}] \\ &= \exp[-2.8563] \\ &= .0575 \text{ ppm.} \end{aligned}$$

DETAILS OF RELATIONSHIP BETWEEN T-TEST AND ACTION LEVEL

To relate the formula for the Action level back to a t-test, notice that if we wished to compare a newly obtained observation--in this case the logarithm of the average of three grab samples (denoted by x_0)--to the previously obtained mean logarithm (\bar{x}), we would calculate the t statistic

$$(x_0 - \bar{x}) / \sqrt{s^2 + s^2/n} \quad (2)$$

and compare it to a table t value. That is, we would take action if the calculated statistic (2) exceeded the table t-value corresponding to the upper 95th percentile with $n-1$ degrees of freedom. Note that under the square root sign we have $s^2 + s^2/n$ since s^2 and s^2/n are the variances of x_0 and \bar{x} , respectively, and the variance of the difference ($x_0 - \bar{x}$) is the sum of the variances.

The following sequence of formula shows the equivalence of Formula (1) and (2). From (2) we take action if

$$x_0 - \bar{x} / \sqrt{s^2 + s^2/n} > t$$

But this expression is equivalent to the following:

$$\begin{aligned} x_0 - \bar{x} &> t * \sqrt{s^2 + s^2/n} , \\ x_0 &> \bar{x} + t * \sqrt{s^2 + s^2/n} , \\ \exp(x_0) &> \exp[\bar{x} + t * \sqrt{s^2 + s^2/n}] . \end{aligned} \quad (3)$$

Since x_0 is the logarithm of the average of the new set of 3 grab-samples, $\exp(x_0)$ is simply the average of the new set of samples. Thus, we take action if the new mean exceeds the right side of formula (3). In other words, the right side of Formula (3), which is equivalent to (1), is the "Action Level".

ADJUSTMENT FOR UPSTREAM CONTAMINATION

A potential problem is that the comparison of each new daily downstream average to the previously computed Action Level makes no allowance for possible upstream contamination. One way to eliminate this problem would be to base the comparison on the difference between the upstream and the downstream averages when the upstream average exceeds the detection limit. Although every upstream measurement obtained so far has been below the detection limit, the procedure would be in place to adjust for upstream contamination if it occurs.

III

GRAND RIVER MONITORING PROGRAM

1. Diamond shall monitor the Grand River by sampling at two designated locations adjacent to the Site. The locations are described below and designated on the map in Appendix B. The locations are hereinafter referred to as the "river sampling locations." The designated locations are:

- (A) Upstream of the Site, at the Route 20 bridge, and,
- (B) Downstream of the Site, approximately 1,000 feet beyond Diamond's pipe bridge, and above the City of Painesville Wastewater Treatment Plant.

2. In accordance with the sampling procedures set forth in Appendix B, three (3) grab samples shall be taken at equal time intervals at both river sampling locations over a six-hour period and analyzed individually in accordance with Appendix A. A Grand River Monitoring Log Sheet shall be maintained in accordance with Appendix B. Log Sheets shall detail sampling results, weather conditions during sampling, water level, daily precipitation, and appearance of the Grand River, and shall be signed by the sampling team members.

3. The Grand River water samples shall be analyzed for total chromium, hexavalent chromium and pH in accordance with Appendix A.

4. Sampling at the river sampling locations shall be performed monthly for the first ten-year period and quarterly for the succeeding 20-year period, subject to such changes in frequency as may be required by weather conditions or otherwise as provided in Section X.7.

5. An average hexavalent chromium value will be calculated for the three (3) grab samples obtained at the downstream sampling location

for each day of sampling, pursuant to Section III.2. A one-tailed Students 't' test shall be applied to the logarithms of these values at the end of the first two years of the Grand River Monitoring Program in order to determine the upper 95 percent confidence limit value (t_{95}). This value shall represent an "Action Level" for hexavalent chromium.

(Whenever the term Action Level appears it relates solely to measurements of hexavalent chromium.) If the mean value of the three (3) grab samples taken at the downstream location pursuant to Section III.2 at any time subsequent to the first two years of monitoring exceeds the Action Level, Diamond shall implement the Contingency Plan described in Section IV.

6. At the conclusion of the first two years of river monitoring Diamond shall calculate the Action Level and notify U.S. EPA and the Ohio EPA, in writing, of the results of its computation and methods of calculation.

IV

CONTINGENCY PLAN

At any time during the Grand River Monitoring Program described in Section III, should the mean value of the three (3) grab samples taken at the downstream locations exceed the Action Level, Diamond shall initiate the following course of action:

- (A) A series of samples shall be taken at each river sampling location in accordance with Appendix B. This series shall consist of three (3) grab samples taken at equal time intervals at each river sampling location over a six-hour period, commencing on the first working day

T A B L E 1

DATA USED IN THE CALCULATION OF THE ACTION LEVEL
FOR HEXAVALENT CHROMIUM

| OBS | MONTH | DAY | YEAR | REPLICATES | | | AVERAGE |
|-----|-------|-----|------|------------|------|------|---------|
| | | | | 1 | 2 | 3 | |
| 1 | 8 | 11 | 83 | 0.01 | ND | 0.01 | .007 |
| 2 | 9 | 13 | 83 | ND | ND | ND | .005 |
| 3 | 10 | 20 | 83 | 0.02 | 0.03 | 0.03 | .027 |
| 4 | 11 | 17 | 83 | ND | ND | ND | .005 |
| 5 | 12 | 21 | 83 | 0.08 | 0.07 | 0.08 | .077 |
| 6 | 2 | 14 | 84 | ND | ND | ND | .005 |
| 7 | 3 | 13 | 84 | 0.04 | 0.03 | 0.04 | .037 |
| 8 | 4 | 24 | 84 | 0.01 | 0.02 | 0.01 | .013 |
| 9 | 5 | 15 | 84 | ND | 0.01 | ND | .007 |
| 10 | 6 | 12 | 84 | 0.02 | 0.03 | 0.03 | .027 |
| 11 | 7 | 18 | 84 | 0.02 | 0.02 | 0.02 | .020 |
| 12 | 8 | 24 | 84 | 0.04 | 0.03 | 0.04 | .037 |
| 13 | 9 | 13 | 84 | 0.02 | 0.02 | 0.02 | .020 |
| 14 | 10 | 9 | 84 | 0.01 | 0.01 | 0.01 | .010 |
| 15 | 11 | 14 | 84 | ND | ND | ND | .005 |
| 16 | 12 | 20 | 84 | 0.02 | 0.02 | 0.02 | .020 |
| 17 | 1 | 29 | 85 | 0.03 | 0.03 | 0.04 | .037 |
| 18 | 2 | 26 | 85 | ND | ND | ND | .005 |
| 19 | 3 | 27 | 85 | 0.01 | 0.01 | 0.01 | .010 |
| 20 | 4 | 23 | 85 | 0.02 | 0.02 | 0.02 | .020 |
| 21 | 5 | 21 | 85 | 0.01 | 0.02 | 0.02 | .017 |
| 22 | 6 | 27 | 85 | 0.02 | 0.02 | 0.02 | .020 |
| 23 | 7 | 9 | 85 | 0.02 | 0.02 | 0.02 | .020 |

P 611 591 168
BICKNEEL (5HE-12)

RECEIPT FOR CERTIFIED MAIL

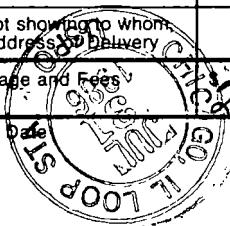
NO INSURANCE COVERAGE PROVIDED
NOT FOR INTERNATIONAL MAIL

(See Reverse)

★ U.S.G.P.O. 1983-403-517

PS Form 3800, Feb. 1982

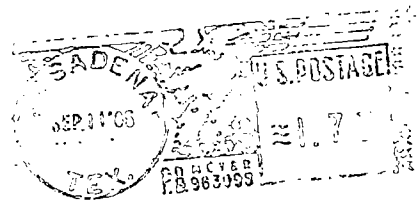
| | |
|---|--------------------------|
| Sent to Mr. Thomas Stang | |
| Chemical Unit Manager | |
| Environmental and Safety Ser | |
| Diamond Shamrock Chemicals CO | |
| 1149 Ellsworth Drive | |
| Postage | Pasadena, Texas 77501.56 |
| Certified Fee | 75 |
| Special Delivery Fee | |
| Restricted Delivery Fee | |
| Return Receipt Showing to whom and Date Delivered | 70 |
| In receipt showing to whom, date, and Address for Delivery | |
| TOTAL Postage and Fees | 22.01 |
| Postmark or Date | |





Diamond Shamrock
Chemicals Company

1149 Ellsworth Drive
Pasadena, Texas 77501



Director
Waste Management Division
U. S. Environmental Protection Agency
Region V (5HE-12)
230 S. Dearborn Street
Chicago, Illinois 60605

5H-12

CERTIFIED

P 188 761 985

MAIL